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Mizoroki−Heck Reaction of (1-Fluorovinyl)methyldiphenylsilane with Aryl Iodides

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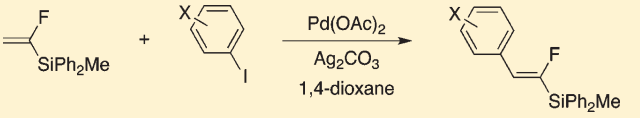
Supporting Information

ABSTRACT: The Mizoroki-Heck reaction of (1-fluorovinyl)-methyldiphenylsilane with a variety of aryl iodides was accomplished under the conditions composing $Pd(OAc)_2$, Ag_2CO_3 and MS 4 Å in 1,4-dioxane to give the corresponding (*E*)-*β*-aryl-(*α*-fluorovinyl)methyldiphenylsilanes with excellent stereoselectivity.



The Mizoroki−Heck reaction has proven to be a powerful tool for the arylation of olefins in organic synthesis.[1] Although a wide range of olefins containing various substituents can participate in the reaction,[2] very few reports concerning the use of fluoroolefins are available.[3] Additionally, the Mizoroki−Heck reaction of vinylsilanes is also understood to be difficult because of its tendency toward elimination of the silyl moiety instead of hydrogen.[4] Hence, to the best our knowledge, there exist no reports concerning the use of silylated fluoroolefins for this reaction. Recently, much effort has been exerted to introduce the fluorine into organic molecules owing to its remarkable effects on their structure, stability, reactivity, and biological activity.[5] Consequently, the stereoselective synthesis of fluoroolefins containing a functional group also remains one of the challenging subjects. We have recently reported an easy preparation of (1-fluorovinyl)methyldiphenylsilane and its application for the construction of a variety of fluorovinyl compounds.[6,7] From another synthetic point of view, this silane would be an attractive candidate for the Mizoroki−Heck reaction. We report herein the first example of the Mizoroki−Heck reaction of silylated fluoroolefin and a synthetic application of the resulting coupling products to transform the corresponding *cis*-*β*-fluorostyrene derivative.

Our investigation started by using (1-fluorovinyl)methyldiphenylsilane **1** and 4′-iodoacetophenone **2a** as a model compound in order to explore the viability on the Mizoroki−Heck reaction. In our early experiment, the reaction in the presence of 10 mol % of $Pd(OAc)_2$ and Ag_2CO_3 (3 equiv) in DMF at 25 °C for 2 h led to the desired product **3a** albeit in 25% yield and with low stereoselectivity (*E*/*Z* = 60/40) along with **1** and some byproduct.[8] For the complete consumption of the unreacted **1**, the longer reaction times caused **3a** to decompose and decrease the yield by contrast. It is noteworthy that when the reaction was conducted at an elevated temperature (50 °C), the reaction was complicated to afford none of **3a**. These unfortunate observations compelled us to continue examinations of a wide range of reaction factors such as Pd catalyst, a base, a solvent, temperature, and an additive.

Some results are shown in Table 1, and the optimal conditions were eventually obtained in entry 13. The reaction well proceeded giving the desired product **3a** in 72% yield with excellent stereoselectivity (*E*/*Z* = 98:2). The *E*/*Z* stereochemistry was assigned on the basis of the coupling constant of ^{1}H NMR and ^{19}F NMR of the product **3a**. The *J* value of 50.3 Hz between the vinylic proton and the fluorine atom indicated the corresponding *E*-configuration. The introduced aryl group is situated at the *trans* position toward the bulky methyldiphenylsilyl group. This *trans* relationship between the aryl and the silyl group is similar to that of the aryl and acyl groups in the Mizoroki−Heck reaction using 3-fluoro-3-buten-2-one.[3d] The reason for the excellent *E*-stereoselectivity should be attributed to the contribution of the stable conformer **A** prior to the required *syn* elimination (Scheme 1).

It is worth noting that the combinatorial conditions of $Pd(OAc)_2$ (10 mol %) and Ag_2CO_3 (3 equiv) in dioxane at 90 °C are essential for the successful reaction. The use of other bases, Pd sources, and different solvents uniformly failed to improve the yield (entries 2−10). The lower loading of Ag_2CO_3 (1−2 equiv) and $Pd(OAc)_2$ (5 mol %) resulted in the lower yields (entries 14−16). Although the role of MS4 Å is not clear at present, it might remove a trace amount of water probably generated from decomposition of H_2CO_3 resulted from Ag_2CO_3 in the reaction mixture.

Table 2 shows the scope of the Mizoroki−Heck reaction of aryl iodides using **1**. The results were almost independent of the position of the aromatic ring as well as the nature of the substituents. The chemical yield of the reaction was typically good to high. The stereoselectivity of the reaction was excellent except for **3d**.[9] Functional groups such as esters, ethers, a nitro, a cyano, and halogens were well tolerated. Unfortunately, no heteroaryl iodides such as 2-iodothiophene and 2-iodopyridine participated in the reaction. Moreover, 4′-bromoacetophenone as an aryl bromide was found to be unreactive for the reaction. In these cases, both of the starting materials were almost recovered intact.

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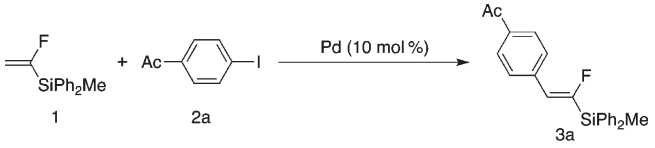
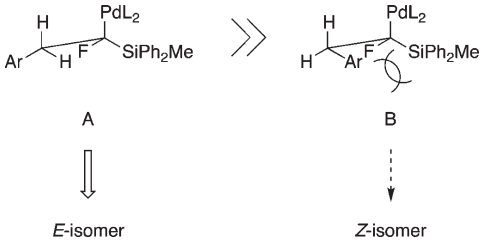
Table 1. Optimization of Reaction Conditions for the Mizoroki–Heck Reaction of 1[a]



entry	Pd (10 mol %)	base (equiv)	solvent	temp/°C	time/h	additive	yield[b]/%	E/Z[c]
1	$Pd(OAc)_2$	Ag_2CO_3 (3)	DMF	25	2	none	25	60/40
2	$Pd(OAc)_2$	NaOAc (3)	DMF	50	12	none	trace	
3	$Pd(OAc)_2$	TEA (3)	DMF	100	12	none	0	
4	$PdCl_2$	$A_{g2}CO_3$ (3)	DMF	50	10	none	0	
5	$Pd(PPh_3)_4$	Ag_2CO_3 (3)	DMF	50	12	none	0	
6	$Pd(OAc)_2$	Ag_2CO_3 (3)	DMSO	100	12	none	0	
7	$Pd(OAc)_2$	Ag_2CO_3 (3)	NMP	100	12	none	0	
8	$Pd(OAc)_2$	Ag_2CO_3 (3)	DMI	100	10	none	0	
9	$Pd(OAc)_2$	Ag_2CO_3 (3)	MeCN	50	12	none	0	
10	$Pd(OAc)_2$	Ag_2CO_3 (3)	THF	60	12	none	0	
11	$Pd(OAc)_2$	$A_{g2}CO_3$ (3)	dioxane	90	12	none	40	98/2
12	$Pd(OAc)_2$	Ag_2CO_3 (4)	dioxane	90	10	MS 4 Å	72	98/2
13	$Pd(OAc)_2$	Ag_2CO_3 (3)	dioxane	90	12	MS 4 Å	72	98/2
14	$Pd(OAc)_2$	Ag_2CO_3 (2)	dioxane	90	12	MS 4 Å	62	98/2
15	$Pd(OAc)_2$	Ag_2CO_3 (1)	dioxane	90	12	MS 4 Å	48	98/2
16[d]	$Pd(OAc)_2$	Ag_2CO_3 (3)	dioxane	90	20	MS 4 Å	60	97/3
17	$Pd(OAc)_2$	Ag_2CO_3 (3)	dioxane	70	10	MS 4 Å	56	99/1

[a] The reactions were carried out in a 0.2 mmol scale with 1 mL of a solvent. [b] Isolated yield. [c] Determined by GC–MS. [d] $Pd(OAc)_2$ (5 mol %) was used.

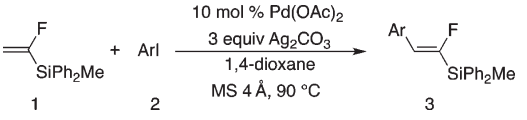
Scheme 1



To illustrate the synthetic scope of this methodology, we briefly attempted to modify the resulting product **3f** (Scheme 2). Our choice was the stereoselective synthesis of the corresponding *cis*-β-fluorostyrene **4f**. If this transformation proceeds with complete retention of the configuration of the double bond, an overall reaction should provide a new stereoselective approach to *cis*-β-fluorostyrene derivatives.[10] As expected, the fluoride ion-assisted desilylation–protonation smoothly proceeded giving the desired **4f**; however, the purification of **4f** from the crude reaction mixture on silica gel column chromatography proved to be more difficult due to their very close R_f values between **4f** and impurities. To overcome this problem, the transformation was achieved by treatment with potassium *tert*-butoxide (*t*-BuOK) in DMSO. The sequentially successful purification of **4f** on silica gel column chromatography was performed to afford the desired **4f** in 99% yield.

In summary, we have developed the Mizoroki–Heck reaction of silylated fluoroolefin **1** with various aryl iodides in good to high yields for the first time. The desilylation–protonation reaction of the product smoothly proceeds giving the corresponding β-fluorostyrene derivative with very high stereoselectivity. This protocol should offer additional opportunities to be of help in fluoroorganic synthesis.

Table 2. Scope of Aryl Iodides[a]



entry	ArI	3	time/h	yield[b]/%	E/Z[c]
1	$4\text{-}AcC_6H_4I$	**3a**	4	72	98/2
2	$4\text{-}EtOC(=O)C_6H_4I$	**3b**	2	63	99/1
3	$4\text{-}O_2NC_6H_4I$	**3c**	4	81	96/4
4	$4\text{-}NCC_6H_4I$	**3d**	3	63	93/7
5	$4\text{-}CF_3C_6H_4I$	**3e**	5	77	97/3
6	$4\text{-}MeOC_6H_4I$	**3f**	5	61	97/3
7	$2\text{-}FC_6H_4I$	**3g**	19	70	98/2
8	$2\text{-}ClC_6H_4I$	**3h**	4	88	97/3
9	$2\text{-}BrC_6H_4I$	**3i**	3	85	98/2
10	$2\text{-}MeOC(=O)C_6H_4I$	**3j**	2	60	98/2
11	$2\text{-}EtC_6H_4I$	**3k**	6	65	98/2
12	$3\text{-}MeOC_6H_4I$	**3l**	4	78	97/3
13	$2,4\text{-}Me_2C_6H_3I$	**3m**	18	67	98/2
14	C_6H_5I	**3n**	6	72	96/4

[a] The reactions were carried out in a 0.2 mmol scale with 1 mL of 1,4-dioxane at 90 °C. [b] Isolated yield. [c] Determined by GC–MS.

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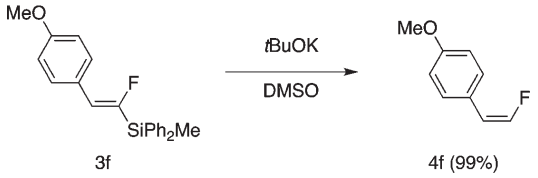
Scheme 2. Transformation of 3f



3f 4f (99%)

EXPERIMENTAL SECTION

General Information. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured in $CDCl_3$ solutions. Chemical shifts were given by δ relative to that of an internal Me_4Si (TMS) for ^{1}H NMR and ^{13}C NMR spectra. Chemical shifts were given by δ relative to that of $CFCl_3$ for ^{19}F NMR spectra using an internal $CF_3C_6H_5$ (benzotrifluoride) or C_6F_6. Infrared (IR) spectra are reported in cm^{-1}. Melting points are uncorrected.

(*E*)-[1-Fluoro-2-(4′-acetylphenyl)vinyl]methyldiphenylsilane (3a). A 25 mL two-necked flask equipped with a magnetic stir bar, a stopcock, and a three-way stopcock was charged with **1** (47.5 mg, 0.196 mmol), **2a** (96.4 mg, 0.391 mmol), Ag_2CO_3 (162.1 mg, 0.606 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), and powdered MS4 Å (ca. 160 mg) in 1,4-dioxane (1 mL), successively. The reaction mixture was heated at 90 °C. When the reaction was completed for 4 h as monitored by GC−MS, the reaction was cooled to room temperature. The reaction mixture was filtered off through Celite pad with ether. After the filtrate was added with water, the organic layer was separated. An additional extraction with hexane/EtOAc = 3/1 was repeated twice. The combined organic solution was dried over Na_2SO_4 and concentrated in vacuo. The resulting oily residue was first purified by column chromatography (silica gel, hexane/EtOAc = 10/1) to give the desired compound **3a** along with a small amount of impurities. The resulting oily residue was additionally purified by bulb-to-bulb distillation to give pale yellow solid (50.9 mg, 72%): mp 92.1−93.5 °C; IR (KBr) 3069, 1680, 1601, 1489, 1355, 1266, 1184, 1115, 1044, 796, 736, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (3H, s), 2.59 (3H, s), 5.97 (1H, d, J = 50.3 Hz), 7.36−7.49 (6H, m), 7.60−7.66 (6H, m), 7.90 (2H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.0 (d, J = 1.2 Hz), 26.6, 122.4 (d, J = 1.9 Hz), 128.2, 128.5, 129.3 (d, J = 8.1 Hz), 130.2, 133.0 (d, J = 1.2 Hz), 135.0, 135.9 (d, J = 2.5 Hz), 137.8 (d, J = 2.5 Hz), 169.4 (d, J = 295.8 Hz), 197.5; ^{19}F NMR ($CDCl_3$, 283 MHz) δ −108.6 (d, J = 50.3 Hz); GC−MS m/z 360 (3, M$^+$), 344 (7), 281 (8), 266 (14), 201 (59), 181 (22), 139 (100), 105 (19), 91 (44). Anal. Calcd for $C_{23}H_{21}FOSi$: C, 76.63; H, 5.87. Found: C, 76.64; H, 5.89.

(*E*)-[1-Fluoro-2-[4′-(ethoxycarbonyl)phenyl]vinyl]methyldiphenylsilane (3b): white solid; yield 63%; mp 71.1−72.7 °C; IR (KBr) 3066, 2974, 1708, 1606, 1427, 1286, 1180, 1109, 1051, 1017, 784, 734, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (3H, s), 1.39 (3H, t, J = 7.16 Hz), 4.37 (2H, q, J = 7.16 Hz), 5.97 (1H, d, J = 50.7 Hz), 7.37−7.51 (6H, m), 7.57−7.68 (6H, m), 7.98 (2H, d, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.0, 14.3, 60.9, 122.5 (d, J = 1.8 Hz), 129.1 (d, J = 8.1 Hz), 129.3 (d, J = 2.5 Hz), 129.6, 130.2, 133.0, 135.0, 137.5 (d, J = 2.5 Hz), 166.3, 169.1 (d, J = 295.2 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −109.2 (d, J = 50.7 Hz); GC−MS (EI, m/z, 70 eV) 348 (21), 286 (5), 255 (26), 231 (60), 201 (89), 169 (25), 139 (100), 105 (30), 91 (81), 77 (17). Anal. Calcd for $C_{24}H_{23}FO_2Si$: C, 73.81; H, 5.94. Found: C, 74.00; H, 6.02.

(*E*)-[1-Fluoro-2-[4′-(nitrophenyl)vinyl]methyldiphenylsilane (3c): pale yellow solid; yield 81%; mp 87.9−89.0 °C; IR (KBr) 3068, 1633, 1597, 1521, 1428, 1342, 1116, 1108, 1058, 824, 795, 735, 674 cm^{-1}; H NMR ($CDCl_3$, 300 MHz) δ 0.82 (3H, s), 5.99 (1H, d, J = 49.4 Hz), 7.37−7.53 (6H, m), 7.63 (4H, dd, J = 7.7, 1.8 Hz), 7.68 (2H, d, J = 8.8 Hz), 8.17 (2H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.0, 121.3 (d, J = 1.9 Hz), 123.7, 128.2, 129.8 (d, J = 8.7 Hz), 130.3, 132.5 (d, J = 1.2 Hz), 135.0, 139.5 (d, J = 3.1 Hz), 146.6 (d, J = 3.1 Hz), 171.0 (d, J = 299.0 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −113.6 (d, J = 49.4 Hz); GC−MS (EI, m/z, 70 eV) 347 (5), 286 (4), 255 (23), 231 (55), 201 (81), 178 (21), 165 (25), 139 (100), 105 (32), 91 (95). Anal. Calcd for $C_{21}H_{18}FNO_2Si$: C, 69.40; H, 4.99; N 3.85. Found: C, 69.33; H, 4.96; N, 3.83.

(*E*)-[1-Fluoro-2-(4′-cyanophenyl)vinyl]methyldiphenylsilane (3d): pale yellow solid; yield 63%; mp 109.0−110.9 °C; IR (KBr) 2229, 1588, 1505, 1488, 1428, 1255, 1109, 1049, 835, 800, 783, 733, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (3H, s), 5.93 (1H, d, J = 49.6 Hz), 7.36−7.51 (7H, m), 7.55−7.66 (7H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.1, 110.9 (d, J = 3.1 Hz), 118.8, 121.3 (d, J = 1.9 Hz), 128.2, 129.6 (d, J = 8.7 Hz), 130.3, 132.1, 132.6, 135.0, 137.6 (d, J = 3.1 Hz), 170.4 (d, J = 297.7 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −107.0 (d, J = 49.6 Hz); GC−MS (EI, m/z, 70 eV) 343 (2, M$^+$), 280 (4), 265 (15), 250 (14), 227 (7), 201 (66), 179 (15), 139 (100), 105 (19), 91 (47); HRMS (FAB, m/z) calcd for $C_{22}H_{19}NFSi$ 344.1295, found 344.1271.

(*E*)-[1-Fluoro-2-[4′-(trifluoromethyl)phenyl]vinyl]methyldiphenylsilane (3e): colorless oil; yield 77%; IR (neat) 3071, 1617, 1489, 1430, 1326, 1168, 1115, 1068, 829, 794, 728, 698, 671 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (3H, s), 5.96 (1H, d, J = 50.1 Hz), 7.36−7.47 (7H, m), 7.52−7.68 (7H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.96, 122.0 (d, J = 1.3 Hz), 125.3 (q, J = 3.7 Hz), 124.1 (q, J = 277.2 Hz), 128.2, 129.4 (d, J = 8.1 Hz), 129.6 (d, J = 2.5 Hz), 130.0 133.1 (d, J = 1.9 Hz), 135.0, 136.6 (dq, J = 3.1, 1.3 Hz), 169.2 (d, J = 294.6 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −64.0, −109.5 (d, J = 50.1 Hz); GC−MS (EI, m/z, 70 eV) 386 (1, M$^+$), 308 (10), 293 (11), 246 (20), 227 (55), 201 (92), 151 (55), 139 (100), 105 (41), 91 (76). Anal. Calcd for $C_{22}H_{18}F_4Si$: C, 68.37; H, 4.69. Found: C, 68.66; H, 4.74.

(*E*)-[1-Fluoro-2-(4′-methoxyphenyl)vinyl]methyldiphenylsilane (3f): white solid; yield 61%; mp 47.1−49.0 °C; IR (KBr) 3011, 1606, 1506, 1428, 1251, 1180, 1117, 1044, 874, 829, 739, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (3H, s), 3.80 (3H, s), 5.87 (1H, d, J = 51.8 Hz), 6.84 (2H, d, J = 9.0 Hz), 7.34−7.46 (6H, m), 7.15 (2H, J = 8.8 Hz), 7.63 (4H, dd, J = 7.7, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.81 (d, J = 1.2 Hz), 55.2, 113.9, 123.0 (d, J = 1.3 Hz), 126.3 (d, J = 2.5 Hz), 128.0, 129.9, 130.7 (d, J = 8.1 Hz), 133.7 (d, J = 1.2 Hz), 135.0, 159.1 (d, J = 3.1 Hz), 165.2 (d, J = 286.5 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −117.3 (d, J = 51.8 Hz); GC−MS (EI, m/z, 70 eV) 348 (19, M$^+$), 286 (5), 255 (26), 231 (57), 201 (83), 178 (20), 165 (25), 139 (100), 105 (29), 91 (79). Anal. Calcd. for $C_{22}H_{21}FOSi$: C, 75.82; H, 6.07. Found: C, 75.82; H, 6.08.

(*E*)-[1-Fluoro-2-[2′-(fluorophenyl)vinyl]methyldiphenylsilane (3g): colorless oil; yield 70%; IR (neat) 3071, 1579, 1482, 1429, 1231, 1117, 1100, 1054, 793, 755, 727, 670 cm^{-1}; H NMR ($CDCl_3$, 300 MHz) δ 0.80 (3H, s), 6.31 (1H, d, J = 51.1 Hz), 6.98−7.04 (1H, m), 7.06−7.15 (1H, m), 7.17−7.25 (1H, m), 7.78−7.47 (6H, m), 7.64 (4H, dd, J = 1.8, 7.5 Hz), 7.93−8.02 (1H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.9, 114.4 (dd, J = 6.8, 1.8 Hz), 115.1 (d, J = 21.1 Hz), 121.1 (dd, J = 11.9, 2.5 Hz), 124.2 (d, J = 19.9 Hz), 128.1, 129.3 (dd, J = 8.7, 1.9), 130.1, 131.1 (dd, J = 13.7, 2.5 Hz) 133.2, 135.0, 159.3 (dd, J = 249.8, 1.2 Hz), 168.5 (dd, J = 293.3, 2.5 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −117.6 (ddd, J = 9.3, 6.1, 6.1), −111.3 (dd, J = 51.1, 6.1 Hz); GC−MS (EI, m/z, 70 eV) 336 (0.5, M$^+$), 254 (49), 239 (28), 201 (86), 178 (59), 165 (28), 152 (24), 139 (100), 105 (30), 91 (76). Anal. Calcd for $C_{21}H_{18}F_2Si$: C, 74.97; H, 5.39. Found: C, 75.13; H, 5.39.

(*E*)-[1-Fluoro-2-(2′-chlorophenyl)vinyl]methyldiphenylsilane (3h): colorless oil; yield 88%; IR (neat) 3070, 1589, 1429, 1254, 1115, 1052, 794, 728, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (3H, s), 6.41 (1H, d, J = 50.5 Hz), 7.13−7.27 (2H, m), 7.32−7.48 (7H, m), 7.65 (4H, dd, J = 7.3, 1.5 Hz), 7.96 (1H, dd, J = 7.7, 1.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.93 (d, J = 1.3 Hz), 119.1 (d, J = 2.5 Hz), 126.7, 128.1, 128.8 (d, J = 1.2 Hz), 129.4, 130.1, 131.1 (d, J = 2.5 Hz), 131.3 (d, J = 12.4 Hz), 132.7 (d, J = 1.2 Hz), 133.2 (d, J = 1.2 Hz), 135.0, 168.2 (d, J = 294.6 Hz); ^{19}F NMR

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($CDCl_3$, 283 MHz) δ −113.3 (d, J = 50.5 Hz); GC−MS (EI, m/z, 70 eV) 352 (0.1, M^+), 254 (21), 239 (5), 223 (5), 212 (10), 201 (53), 178 (32), 139 (100), 105 (19), 91 (50). Anal. Calcd. for $C_{21}H_{18}ClFSi$: C, 71.47; H, 5.14. Found: C, 71.56; H, 5.13.

(*E*)-[1-Fluoro-2-(2′-bromophenyl)vinyl]methyldiphenylsilane (3i): colorless oil; yield 85%; IR (neat) 3070, 1589, 1461, 1429, 1254, 1115, 1057, 1045, 793, 728, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.81 (3H, s), 6.37 (1H, d, J = 50.1 Hz), 7.04−7.14 (1H, m), 7.23−7.32 (1H, m), 7.36−7.48 (6H, m), 7.55 (1H, dd, J = 8.1, 1.3 Hz), 7.65 (4H, dd, J = 7.7, 1.8 Hz), 7.93 (1H, dd, J = 7.7, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.98 (d, J = 1.2 Hz), 121.9 (d, J = 3.2 Hz), 123.4 (d, J = 1.2 Hz), 127.3, 128.1, 129.0 (d, J = 1.3 Hz), 130.1, 131.4 (d, J = 20.5 Hz), 132.67, 132.73 (d, J = 12.4 Hz), 133.1 (d, J = 1.2 Hz), 135.0, 167.9 (d, J = 294.6 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −114.0 (d, J = 50.1 Hz); GC−MS (EI, m/z, 70 eV) 397 (0.8, M^+), 317 (7), 302 (10), 255 (28), 239 (44), 223 (9), 201 (98), 178 (71), 139 (100), 91 (68). Anal. Calcd for $C_{21}H_{18}BrFSi$: C, 63.48; H, 4.57. Found: C, 63.71; H, 4.58.

(*E*)-[1-Fluoro-2-[2′-(methoxycarbonyl)phenyl]vinyl]methyldiphenylsilane (3j): colorless oil; yield 60%; IR (neat) 1721, 1598, 1429, 1080, 794, 728 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.81 (3H, s), 3.75 (3H, s), 6.77 (1H, d, J = 50.3 Hz), 7.25−7.35 (1H, m), 7.35−7.51 (8H, m), 7.66 (4H, dd, J = 1.8, 7.5 Hz), 7.82−7.92 (1H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.0 (d, J = 1.2 Hz), 51.9, 121.6 (d, J = 3.2 Hz), 123.4 (d, J = 1.2 Hz), 127.3, 128.1, 129.0 (d, J = 1.3 Hz), 130.0, 131.3 (d, J = 9.4 Hz), 131.7, 133.3 (d, J = 4.4 Hz), 133.4 (d, J = 1.3 Hz), 135.1, 166.6 (d, J = 292.1 Hz), 167.8; ^{19}F NMR ($CDCl_3$, 283 MHz) δ −116.4 (d, J = 50.3 Hz); GC−MS (EI, m/z, 70 eV) 376 (0.2, M^+), 360 (4), 299 (37), 197 (64), 179 (100), 151 (37), 139 (34), 129 (41), 101 (25), 91 (42). Anal. Calcd. for $C_{23}H_{21}O_2FSi$: C, 73.37; H, 5.62. Found: C, 73.66; H, 5.76.

(*E*)-[1-Fluoro-2-(2′-ethylphenyl)vinyl]methyldiphenylsilane (3k): colorless solid; yield 65%; mp 46.0−48.0 °C; IR (KBr) 3068, 2965, 1588, 1476, 1428, 1250, 1118, 1044, 757, 736, 700, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80 (3H, s), 1.08 (3H, t, J = 7.52 Hz), 2.51 (2H, q, J = 7.52 Hz), 6.12 (1H, d, J = 50.6 Hz), 7.11−7.22 (2H, m), 7.36−7.47 (7H, m), 7.64 (4H, dd, J = 2.0, 7.7 Hz), 7.75−7.84 (1H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.9, 15.0, 26.9, 121.0 (d, J = 1.3 Hz), 125.9, 128.0 (d, J = 1.2 Hz), 128.1, 128.6, 130.0, 130.2 (d, J = 10.0 Hz), 130.9 (d, J = 2.5 Hz), 133.6 (d, J = 1.9 Hz), 135.0, 141.8, 166.4 (d, J = 290.2 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −116.5 (d, J = 50.6 Hz); GC−MS (EI, m/z, 70 eV) 347 (11, M^+), 346 (35), 253 (6), 206 (23), 201 (61), 197 (48), 191 (12), 139 (100), 129 (26), 91 (22). Anal. Calcd for $C_{23}H_{23}FSi$: C, 79.72; H, 6.69. Found: C, 79.71; H, 6.67.

(*E*)-[1-Fluoro-2-(3′-methoxyphenyl)vinyl]methyldiphenylsilane (3l): colorless oil; yield 78%; IR (neat) 1599, 1428, 1256, 1115, 1050, 792, 670, 727, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.79 (3H, s), 3.79 (3H, s), 5.91 (1H, d, J = 51.0 Hz), 6.98 (1H, dd, J = 2.6, 8.1 Hz), 7.07−7.27 (3H, m), 7.35−7.47 (6H, m), 7.63 (4H, dd, J = 1,8, 7.7) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.9 (d, J = 1.2 Hz), 55.2, 114.0 (d, J = 1.9 Hz), 114.3 (d, J = 8.1 Hz), 121.9 (d, J = 6.9 Hz), 123.3 (d, J = 1.9 Hz), 128.1, 129.3, 130.0, 133.4 (d, J = 1.3 Hz), 134.5 (d, J = 2.4 Hz), 135.0, 159.5, 167.1 (d, J = 291.4 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −112.6 (d, J = 51.0 Hz); GC−MS (EI, m/z, 70 eV) 348 (8, M^+), 332 (4), 269 (9), 254 (41), 201 (73), 178 (37), 165 (18), 139 (100), 105 (26), 91 (70). Anal. Calcd for $C_{22}H_{21}FOSi$: C, 75.82; H, 6.07. Found: C, 75.78; H, 6.08.

(*E*)-[1-Fluoro-2-(2′,4′-dimethylphenyl)vinyl]methyldiphenylsilane (3m): colorless oil; yield 67%; IR (neat) 3070, 1613, 1589, 1429, 1253, 1116, 1053, 793, 728, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.70 (3H, s), 2.15 (3H, s), 2.28 (3H, s), 6.07 (1H, d, J = 49.2 Hz), 6.94−7.01 (2H, m), 7.34−7.45 (6H, m), 7.64 (4H, dd, J = 1.7, 7.5 Hz), 7.69 (1H, d, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.9 (d, J = 1.2 Hz), 19.9, 21.1, 121.0, 126.6, 128.0, 128,4 (d, J = 1.8 Hz), 129.8, 130.0, 130.8, 133.7, 135.0, 135.5, 137.5 (d, J = 1.2 Hz), 165.8 (d, J = 289.0 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −116.4 (d, J = 49.2 Hz); GC−MS (EI, m/z, 70 eV) 347 (3, M^+), 253 (14), 229 (7), 201 (91), 181 (16), 165 (11), 152 (7), 139 (100), 105 (38), 91 (68). Anal. Calcd for $C_{23}H_{23}FSi$: C, 79.72; H, 6.69. Found: C, 79.74; H, 6.71.

(*E*)-(1-Fluoro-2-phenylvinyl)methyldiphenylsilane (3n): colorless oil; yield 72%; IR (neat) 3070, 3051, 3025, 1589, 1447, 1115, 1049, 793, 727, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80 (3H, s), 5.96 (1H, d, J = 50.1 Hz), 7.35−7.47 (7H, m), 7.51−7.58 (2H, m), 7.59−7.67 (7H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.9 (d, J = 1.3 Hz), 123.4 (d, J = 1.9 Hz), 127.8 (d, J = 2.5 Hz), 128.1, 128.4, 129.3 (d, J = 7.4 Hz), 130.0, 133.3 (d, J = 2.5 Hz), 133.4 (d, J = 1.3 Hz), 135.0, 166.9 (d, J = 290.2 Hz); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −106.1 (d, J = 50.1 Hz); GC−MS (EI, m/z, 70 eV) 318 (2, M^+), 302 (5), 255 (11), 239 (31), 225 (39), 201 (97), 178 (84), 139 (100), 105 (30), 91 (56); HRMS (EI, m/z) calcd for $C_{21}H_{19}FSi$ 318.1240, found 318.1209.

(*Z*)-1-Fluoro-2-(4′-methoxyphenyl)ethene (4f)[10a]. A 25 mL two-neck flask equipped with a magnetic stir bar, a stopcock, and a three-way stopcock was charged with **3f** (72.9 mg, 0.209 mmol), *t*-BuOK (34.7 mg, 0.309 mmol), and DMSO (1.0 mL) at room temperature. After the reaction was stirred for 1 h, the reaction mixture was quenched with water. After separation of the organic layer, additional extraction with hexane/EtOAc was repeated twice. The combined organic solution was dried over Na_2SO_4 and concentrated in vacuo. The residual oil was purified by silica gel chromatography (hexane/ether =100/1) to give **4f** as a colorless oil (31.6 mg, 99%): ^1H NMR ($CDCl_3$, 300 MHz) δ 3.81 (3H, s), 5.54 (1H, dd, J = 35.1, 5.3 Hz), 6.59 (1H, dd, J = 82.9, 5.3 Hz), 6.87 (2H, d, J = 8.8 Hz), 7.45 (2H, d, J = 8.8 Hz).

■ ASSOCIATED CONTENT

Supporting Information. ^1H, ^{13}C, and ^{19}F NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org/.

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